



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Takuo SONE et al

Serial No. 10/759,299

Group Art Unit: 1713

Filed: January 20, 2004

For : METHOD OF PRODUCING CONJUGATED DIENE POLYMERS

DECLARATION UNDER RULE 132

I, Takuo Sone, declare that:

I am an inventor of the above-referenced United States Patent Application Serial No. 10/759,299.

I received my Doctor of Material Bioengineering from Tokyo University of Agriculture and Technology in the year of 1995 and I have been employed by JSR Corporation since 1995, wherein I have been engaging mainly in the research and development of various solution-polymerized elastomers.

I have made the following experiment in order to show that the present invention can not be easily conceived from Ikematsu (JP 05051406) or Tsujimoto (JP 8073515) or a combination thereof.

Experiment

Five polymers of Run-1 to Run-5 were prepared in the same manner as described in Example 1 of the specification of the present invention using a catalyst system and a modifying agent shown in Table 1. In this case, Run-1 corresponds to Example 11 of the specification of the present invention using as a modifying agent diethyl adipate described in Ikematsu, and Run-2 and Run-3 correspond to Comparative Examples 1

and 2 of the specification of the present invention, which are supplementary experiments of Tsujimoto, and Run-4 is a supplementary experiment corresponding to Comparative Example 1 of Ikematsu and Run-5 is a supplementary experiment corresponding to Example 3 of Ikematsu. In Run-4 and Run-5, the amounts of the catalyst components added were adjusted so as to match the Mooney viscosity with those of Run-1 to Run-3, and the amount of diethyl adipate added was adjusted so as to be equal to that of Example 11.

A vulcanizate was prepared by using each of the polymers of Run-1 to Run-5 according to the compounding recipe described on page 36 of the specification of the present invention in the same manner as described on page 36, lines 11 to 16 of the specification of the present invention.

The properties of the polymer and the vulcanizate were measured in the same manner as described on pages 35 to 36 of the specification of the present invention to obtain results as shown in Table 2.

Table 1

	Catalyst component(mmol)				Modifying agent (mmol)
	Rare earth element compound	Aluminoxane	Organoaluminium compound	Component (b)	
Run-1 (Example-11)	Nd(Oct) ₃ 0.18	MAO 18.5	Al ⁱ Bu ₂ H 3.9	AlEt ₂ Cl 0.37	Diethyl adipate 3.6
Run-2 (Comparative Example 1)	Nd(Oct) ₃ 0.18	MAO 18.5	Al ⁱ Bu ₂ H 3.9	AlEt ₂ Cl 0.37	-
Run-3 (Comparative Example 2)	Nd(Oct) ₃ 0.18	MAO 4.7	Al ⁱ Bu ₂ H 3.8	AlEt ₂ Cl 0.37	-
Run-4	Nd(Oct) ₃ 0.21	-	Al ⁱ Bu ₂ H 5.6	Al ₂ Et ₃ Cl ₃ 0.42	-
Run-5	Nd(Oct) ₃ 0.21	-	Al ⁱ Bu ₂ H 5.6	Al ₂ Et ₃ Cl ₃ 0.42	Diethyl adipate 3.6

Table 2

	Mooney viscosity (ML ₁₊₄ , 100°C)	Mw/Mn	Cis-1,4- bond (%)	Vinyl-1,4- bond (%)	Cold Flow (mg/min)	TB (MPa)	EB (%)	Rebound resilience (25°C, %)	Wear resistance (index)
Run-1 (Example-11)	38	3.4	96.9	1.2	1.6	26.5	475	65	123
Run-2 (Comparative Example 1)	31	2.2	97	1.1	18.5	26.5	470	62	120
Run-3 (Comparative Example 2)	34	3.6	97	1.1	15.5	25.8	510	56	105
Run-4	34	3.8	95.8	1.2	6.8	26.1	490	52	94
Run-5	36	4.4	95.8	1.2	4.6	26	490	50	89
Run-6 (Comparative Example 3)	-	-	-	-	-	25.7	530	54	100

In Table 2, Run-6 corresponds to Comparative Example 3 of the specification of the present invention and is a standard sample for evaluating the properties of the vulcanizate.

As seen from the comparison of Run-1 with Run-2 and Run-3, the cold flow is considerably improved by conducting the modification reaction with diethyl adipate.

Then, the rebound resilience and the wear resistance are reviewed as the properties of the vulcanizate. In general, it is known that both the properties are dependent upon the molecular weight distribution of the polymer. Also, both the properties are dependent upon the molecular weight of the polymer. They are deteriorated as the molecular weight of the polymer becomes low. The polymer having a wide molecular weight distribution is unfitted for the improvement of the rebound resilience and wear resistance because it has a greater amount of low molecular weight component. Therefore, the rebound resilience and wear resistance become good in the polymer having a narrow molecular weight distribution if the Mooney viscosity is the same level. In fact, as seen from the comparison between Run-2 and Run-3 corresponding to the examples of Tsujimoto, Run-2 having a narrower molecular weight distribution is excellent in the rebound resilience and wear resistance as compared with Run-3.

In Run-1 corresponding to Example 11 of the present invention, the molecular weight distribution (M_w/M_n) is 3.4, which is approximately equal to that of Run-3, but the rebound resilience and wear resistance are excellent as compared with those of Run-2. Since the polymerization conditions in Run-1 are the same as in Run-2, the molecular weight distribution of the polymer before the addition of diethyl adipate is as narrow as 2.2 and also the low molecular weight component is less, and hence when such a polymer is subjected to the

modification reaction with diethyl adipate, the reaction proceeds in a higher efficiency and the low molecular weight component is further decreased and as a result, the rebound resilience and wear resistance are improved. From this fact it is clear that the catalyst system defined in the present invention has a high living property and is very suitable for the modification reaction in a higher reaction efficiency and brings about a high balance the cold flow and the vulcanization properties by the combination with the modification reaction.

Run-4 and Run-5 are the supplementary experiments of Ikematsu as mentioned above. The polymer of Run-4 before the reaction with diethyl adipate has a molecular weight distribution of 3.8 and the polymer of Run-5 obtained by reacting the polymer of Run-4 with diethyl adipate has a molecular weight distribution of 4.4, from which it is clear that the modification reaction with diethyl adipate proceeds. However, the cold flow is 6.8 in Run-4 and 4.6 in Run-5, so that the improving effect of the cold flow is small as compared with Run-1. Also, the rebound resilience and wear resistance in Run-5 are 50 and 89, which are deteriorated as compared with those of Run-4 (52 and 94). This is due to the fact that MAO (methylaluminoxane) is not used in the catalyst system of Ikematsu and the living ratio is low. That is, it is guessed that since the living ratio in the catalyst system of Ikematsu is low, the contribution ratio of low molecular weight component to the modification reaction is low, and hence the cold flow and the rebound resilience and wear resistance are deteriorated due to the influence of widening the molecular weight distribution to 4.4. In the invention of Ikematsu, therefore, it is not always attained that the cold flow and the vulcanization properties are largely improved by simply conducting the modification reaction.

It can be seen from the above experiment that the present invention can not be easily conceived from Ikematsu or Tsujimoto or a combination thereof.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: March 30, 2005 Declarant: Takuo Sone
Takuo Sone